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Quantum-dynamical Modeling of the Rydberg to Valence Excited-State Internal Conversion in Cyclobutanone and Cyclopentanone

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Abstract. In this paper we present 4-state, 5-dimensional Vibronic Coupling Hamiltonians for cyclobutanone and cyclopentanone. Wave packet calculations using these Hamiltonians reveal that for cyclobutanone the $(n,3s)$ to (n,π^*) internal conversion involves direct motion in nuclear modes coupling the two states leading to fast population transfer. For cyclopentanone, internal vibrational energy redistribution is a bottleneck for activating reactive nuclear modes leading to slower population transfer.

1 Introduction

Processes in excited states initiated by short laser pulses can exhibit significant non-ergodic behavior as exemplified by the cycloketones [1,2]. The direct time-scale for the $(n,3s)$ to (n,π^*) transition in these molecules exhibit such effects [2]. A perturbative approach, i.e., Fermi's golden rule, should be able to describe the rate of such a transition

$$w_{m \leftarrow n}(E) = (2\pi/\hbar) |\langle \Psi_m | V | \Psi_n \rangle|^2 \rho_m(E). \quad (1)$$

Here $\rho_m(E)$ is the density of vibrational states of the final electronic state $|\Psi_m\rangle$ and V is the perturbation coupling the two states. Contrary to the expectation of a rise in the rate of transition as $\rho_m(E)$ is increased, the exact opposite trend was observed for the cycloketones [2]. This observation points to a significant coordinate dependence of the coupling matrix element in Eq. 1. To investigate this, we present in here the construction of 4-state, 5-dimensional vibronic coupling Hamiltonians (VCHAM) [3] for cyclobutanone and cyclopentanone and their use in wave packet calculations to investigate the true dynamical nature of the $(n,3s)$ to (n,π^*) transition in these molecules.

2 Computational Methods

Wave packet calculations were performed using the Heidelberg Multi-configuration Time-Dependent Hartree (MCTDH) code [4]. The VCHAMs were fitted on the basis of 1182 and 1273 *ab initio* points for cyclobutanone and cyclopentanone, respectively, with a locally modified version of the VCHFIT program distributed with the Heidelberg MCTDH code.

Quantum chemistry calculations were performed in Gaussian 03 [5], CFOUR [6], and Dalton [7] at the coupled-cluster singles and doubles (CCSD) [8,9] and equation of motion (EOM) or linear

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response CCSD levels of theory. The cc-pVTZ basis set [10] was augmented by a 1s1p1d set of diffuse functions to describe the Rydberg states [11].

3 The Vibronic Coupling Hamiltonian

The VCHAM is given in dimensionless normal mode coordinates obtained at the ground state equilibrium geometry. A subset of modes were chosen such as to describe the significant changes between the equilibrium structure of the ground, (n, π^*) , and $(n, 3s)$ states; ring-pucker (labeled v_1/v_1 for cyclobutanone/cyclopentanone), carbonyl out-of-plane deformation (v_2/v_3), symmetric C-CO-C stretch (v_7/v_8), asymmetric C-CO-C stretch (v_{12}/v_{16}), and C=O stretch (v_{21}/v_{28}).

Fig. 1 and Fig. 2 give examples of the fit between the parameterized VCHAMs and the *ab initio* data. For the ground state of cyclobutanone and cyclopentanone the RMSD between *ab initio* data and fit is 4.97 and 13.9 meV respectively. For the three excited states the RMSD is 8.2 meV and 4.28 meV for cyclobutanone and cyclopentanone respectively.

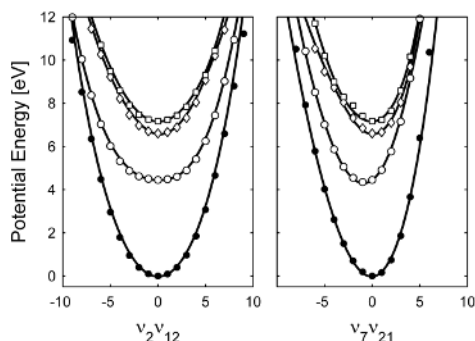


Fig. 1. *Ab initio* points (symbols) for the four lowest states of cyclobutanone along the mode diagonals v_2v_{12} and v_7v_{21} as well as the potential energy surfaces obtained from the fitted VCHAM (lines).

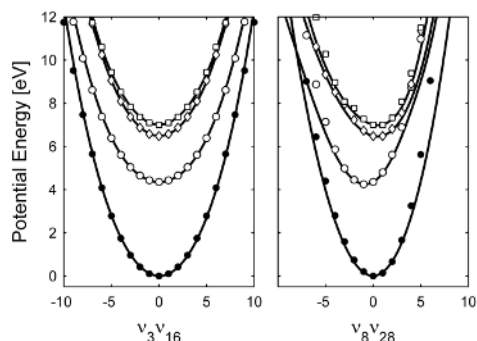


Fig. 2. *Ab initio* points (symbols) for the four lowest states of cyclopentanone along the mode diagonals v_3v_{16} and v_8v_{28} as well as the potential energy surfaces obtained from the fitted VCHAM (lines).

4 Dynamics

Although the potential energy surfaces of cyclobutanone and cyclopentanone are very similar for the five modes included in the VCHAMs as exemplified in Fig. 1 and Fig. 2, very different time-scales for the transition between the initial $(n, 3s)$ and final (n, π^*) state is observed. Fig. 3 shows the diabatic populations of the three excited states following excitation to the $(n, 3s)$ state. The decay of the $(n, 3s)$ population can for both molecules be adequately fitted by a decaying biexponential function with time-constants of 0.95 ps and 6.32 ps for cyclobutanone and 3.99 ps and 81.5 ps for cyclopentanone. The short time-constants are in good correspondence with the ones obtained from time-resolved mass spectrometry of 0.74 ps and 5.30 ps for cyclobutanone and cyclopentanone respectively [2].

A significant difference between the two molecules can be found in the symmetries of their excited states. For cyclobutanone, which belongs to the C_s point group, both the (n, π^*) and the $(n, 3s)$ state belong to the A'' irreducible representation, and it is thus the Franck-Condon active modes v_1 , v_2 , v_7 , and v_{21} belonging to A' , which are responsible for the linear vibronic coupling part of the perturbation operator V of Eq. 1. As a consequence direct motion in the coupling modes occurs right after excitation to the $(n, 3s)$ state and population transfer is fast. On the other hand, for cyclopentanone, which belongs to the C_2 point group, the (n, π^*) state belongs to the A irreducible representation whereas the $(n, 3s)$ state belongs to B . As a consequence it is the non-Franck-Condon

active modes ν_1 , ν_3 , and ν_{16} belonging to B, which are responsible for the linear vibronic coupling. Motion in the coupling modes does therefore not occur until vibrational energy redistribution has transferred energy from the Franck-Condon modes ν_8 and ν_{28} into the coupling modes – a process which is observed to take on the order of 10 ps. As a consequence population transfer is an indirect process and slower than what is observed in the case of cyclobutanone.

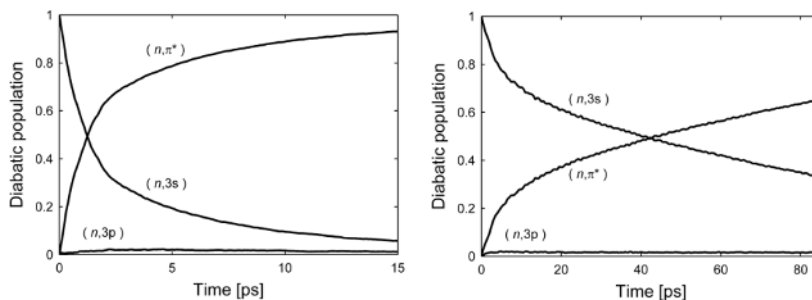


Fig. 3. Diabatic populations of the (n,π^*) , $(n,3s)$, and $(n,3p)$ states as a function of time following excitation to the $(n,3s)$ state for cyclobutanone (left) and cyclopentanone (right).

5 Conclusion

Similar to experiment, wave packet calculations reveal that the $(n,3s)$ to (n,π^*) transition is faster in cyclobutanone compared to cyclopentanone. The difference of time-scales can be explained from the two different mechanisms of internal conversion; one direct where motion in the reactive coupling modes leads to a fast population transfer and one indirect where internal vibrational energy redistribution (IVR) from the non-reactive modes is a bottleneck for activating the reactive coupling modes. In the direct mechanism the transition takes place on a time-scale shorter than that of IVR and thus non-ergodicity prevails. In the indirect mechanism, IVR takes place on a timescale comparable to or slightly shorter than that of the transition and ergodicity somewhat prevails.

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